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LIFETIME OF NANO-STRUCTURED BLACK SILICON FOR PHOTOVOLTAIC APPLICATIONS

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ABSTRACT: In this work, we present recent results of lifetime optimization for nano-structured black silicon and its photovoltaic applications. Black silicon nano-structures provide significant reduction of silicon surface reflection due to highly corrugated nanostructures with excellent light trapping properties. We applied reactive ion etching technology at -20ºC to create nano-structures on silicon samples and obtained an average reflectance below 0.5%. For passivation purposes, we used 37 nm ALD Al_2O_3 films. Lifetime measurements resulted in 1220 µs and to 4170 µs for p- and n-type CZ silicon wafers, respectively. This is promising for use of black silicon RIE nano-structuring in a solar cell process flow.

Keywords: c-Si, black silicon, ALD Al_2O_3, passivation, lifetime, light trapping, nano-structured silicon

1 INTRODUCTION

Nano-textured silicon, known as black silicon, is currently a subject of great interest in photovoltaics [1–4, 5]. It has extremely low surface reflectance, in some cases below 1%, in a broad range of wavelengths and incident angles even with a simple antireflective coating [6, 7]. Reactive plasma etching is a most promising alternative to any other silicon texturing method like wet etching [8–11], plasma immersion ion implantation etching, metal nanoparticles assisted etching and laser induced etching [12–15]. Key advantages of dry plasma silicon structuring are no usage of toxic chemicals, easy morphology control of structure size and shape, less silicon waste and mask-less processing. Solar cells with improved light trapping nano-structures show improved characteristics, such as high open circuit voltage and large short circuit current. However, surface-texturing methods like RIE also induce surface damage and potentially contamination, and therefore increased surface recombination velocity resulting in poor performance of nano-structured solar cells [3, 5, 16, 17]. Thus, effective surface passivation of nano-textured surfaces and optimization of the texturing process towards reduction of surface defect damage is required for further black silicon application in photovoltaics [18–22]. Atomic layer deposition (ALD) of Al_2O_3 is one of the best methods for black silicon passivation, since it has conformal coverage of plane and corrugated surfaces. Thermal ALD of Al_2O_3 leads to high chemical interface quality on crystalline silicon, low density of defect states, and the strongest known field effect due to fixed negative charges [18, 20, 21, 23–32].

2 EXPERIMENT

2.1 Sample Details and Black Silicon Etching

Black silicon nanostructuring was realized on Czochralski (CZ) mono-crystalline Si 4” (100) n- and p-type (1-20 Ωcm) wafers with thickness 350 µm by mask-less reactive ion etching (RIE) in SF_6 and O_2 inductively coupled plasma at -20ºC in DRIE SPTS Pegasus (Fig.1). Prior to final sample preparation, the RIE process was optimized: platen power was reduced from 50 to 10 W to reduce kinetic energy of ions, directed towards the substrate surface; coil power was increased from 2500 to 3000 W to increase homogenous ion plasma density and maintain a stable etch rate; aspect ratio of nanostructures was controlled via the low gas pressure (38 mTorr) which determined the directionality of the ions and the physical etching components by reducing the mean free path of the plasma species; average flow of SF_6 gas (70 sccm) allowed to a stable Si etch rate and high O_2 flow (100 sccm) allowed to passivate Si surface and reduce etch rate. The first samples had shown low lifetime after ALD Al_2O_3 passivation and are not referred in this report. For conducting the experiment we used six silicon wafers of n- and p-type: two wafers had single side RIE processing for 16 min, another two wafers had double sided RIE processing for 16 min on each side and the last two wafer were kept as plain polished references.

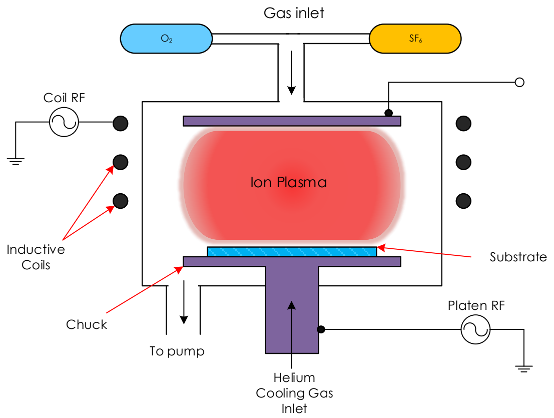

Figure 1: Schematic of inductive coupled plasma system used for RIE

The black silicon nano-structuring process was conducted in the following order as shown on Fig. 2. A sample wafer was loaded in to the ICP RIE chamber and cooled to -20ºC. SF_6 gas was supplied to the chamber and fluorine radicals rapidly attacked the silicon and destroyed native oxide on top of the wafer forming volatile SiF_4. In the next step, oxygen was supplied to the chamber. Oxygen radicals form silicon-oxyfluorine SiF_4+O*=SiO_xF_y at low temperature (-20ºC). SiO_xF_y acts as an etch stop for F* and passivated sample surface. Horizontal planes were more intensively bombarded by ions from plasma while on the vertical sidewalls the ion bombardment was weaker due to directionality of the plasma ions and the sidewalls therefore remained protected from chemical etching by fluorine radical [1-2].

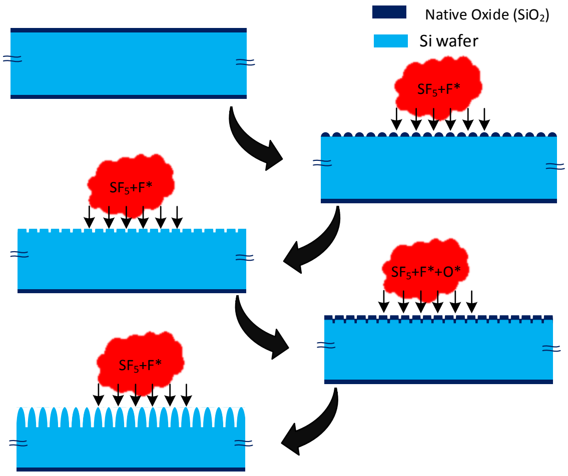

Figure 2: Schematic view of black silicon nanostructures formation

2.2 Surface cleaning and ALD Al_2O_3 passivation

After RIE all samples were cleaned in standard RCA cleaning solutions, RCA1 and RCA2, each with a subsequent HF-dip, rinsed in deionized water and spin dried. Subsequently, wafers were coated with 380 cycles of ALD Al_2O_3 synthesized from trimethylaluminium (TMA) and H_2O. For reference purposes two polished wafers (p- and n-type) were also included in ALD Al_2O_3 passivation procedure. The passivation layers were activated by post-deposition in-situ annealing in N_2 ambient at 375-390 ºC for 30 min. The resulting Al_2O_3 thickness of 37 nm was measured from polished reference samples using ellipsometry. Charge carrier lifetime was measured after annealing with the microwave detected photoconductivity (MDP) method in transient as well as in injection dependent single point modes, and lifetime mapping mode using a MDPmap setup from Freiburg Instruments.

3 RESULTS AND DISCUSSIONS

3.1 Black Silicon SEM Morphology Study

In Fig. 3 scanning electron microscope (SEM) images of the resulting black silicon nano-structures are shown without Al_2O_3 coating. The nanostructure topology consists of slightly rounded conical-like hillocks with average height of 500 nm and average spacing of 250 nm. There is a slight variation in the dimensions of the surface structures. The height of the nanostructures was controlled by etching time with an average etch rate of 30 nm/min.

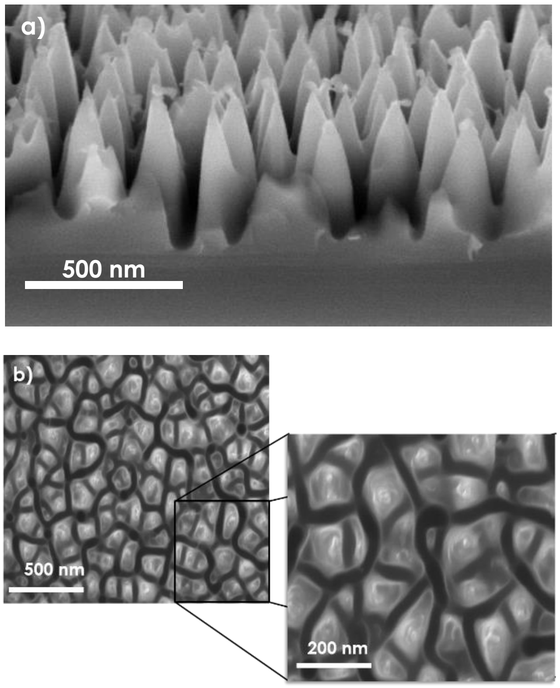

Figure 3: SEM image of the black silicon nano-structure topology processed with plasma assisted mask-less reactive ion etching: a) side view with scale 500 nm, b) top views with scale 500 nm and 200 nm

3.2 Reflectance

The main purpose of nanostructuring is to reduce reflectance and improve light trapping properties of the Si surface [3, 33]. The spectral reflectance of black silicon and polished samples were measured in the wavelength range from 500 to 1100 nm. Fig. 4 shows the reflectance of the samples as a function of wavelength. Photographic images are inserted in the reflectance figure to illustrate the difference between polished and nanostructured samples. It can be seen that polished silicon wafer in average has reflectance of 30%, while the black silicon sample has reflectance below 1% up to 1000 nm. Above 1000 nm the reflectance still remains low but shows a slight increase up to 5% which is still much lower than that of the polished wafer, and this long wavelength reflectance may partly be due to reflectance of the chuck below the silicon sample.

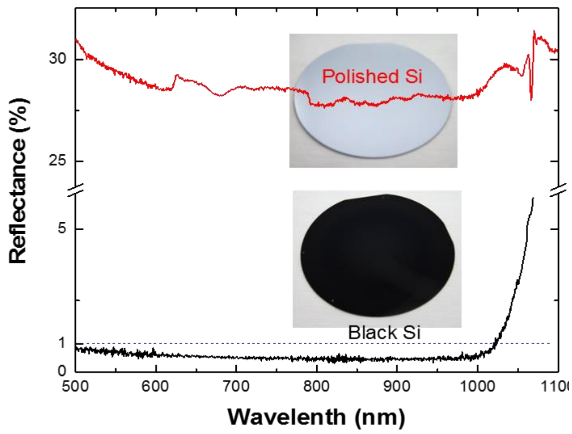

Figure 4: Experimental reflectance spectra of polished and black silicon without Al_2O_3 coating

3.3 Minority Carrier Lifetime

Fig. 5 shows measured effective minority carrier lifetime for p- and n-type wafers for polished as well as for nano-textured samples. MDP measurements were conducted with a MDPmap setup from Freiberg Instruments to determine the effective carrier lifetimes as a function of injection level. The effective minority lifetime is a figure of merit to estimate surface recombination and surface damage [18, 21, 25, 34, 35].

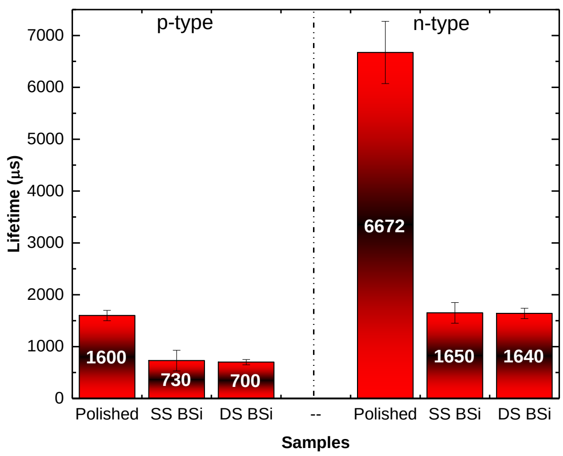

Figure 5: Comparative graph of average lifetime wafer mapping values with standard deviation for p- and n-type silicon samples with polished, single side nanostructured and double side nanostructured black silicon, passivated with ALD Al_2O_3 37 nm film. Legend: SS BSi - single side nanostructured black silicon, DS BSi - double side nano-structured black silicon

For p-type Si wafers, the lifetime difference between polished and textured samples is a factor of two. For some samples we have recorded a lifetime approaching 1 ms and higher, however to report these results additional testing is required. Injection dependent lifetime for p-type samples shown in Fig. 6 confirms stability of above results. A similar tendency is present for n-type samples, however lifetime difference between polished and nanostructured samples is in that case a factor of four.

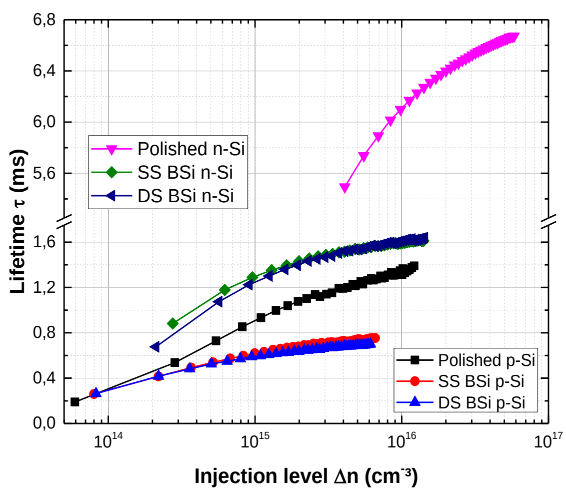

Figure 6: Lifetime dependency on injection level

The surface recombination velocity was calculated from effective minority carrier lifetime from the equation shown in Fig. 6 [25].

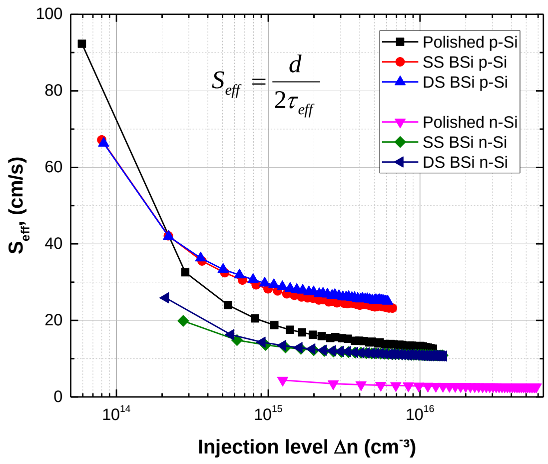

Figure 7: Surface recombination velocity dependencies on injection level

where d is the wafer thickness, τ_{eff} is the measured effective lifetime. Fig. 7 shows the calculated surface recombination velocity as a function of injection level.

4 CONCLUSION

We have presented recent results of effect of reactive ion process optimization for improvement of minority carrier lifetime. The optimized RIE recipe with reduced ion damage of the surface allows us to achieve comparatively high effective lifetime for n- and p-type wafers and for single and double side nano-textured samples. For further investigation of electro-optical properties all samples were passivated with Al_2O_3 and annealed at 375-390ºC for 30 min. The surface morphology of textured samples was studied using SEM, and the optical reflectance was measured with an integrated sphere in the range of 500-1100 nm. Reflectance measurements allow us to evaluate the antireflective properties of nanostructures. With the plasma-assisted mask-less etching method we achieved broad spectral reflectance below 0.5%. Finally, the effective lifetime was measured on all textured and reference polished samples to evaluate the passivation effect and to estimate surface recombination velocity. Our overall results are promising for black silicon fabrication and lifetime improvement to facilitate incorporation in solar cell fabrication.

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